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13. ABSTRACT (Maximum 200 words)  Modulated molecular beam studies have been carried out in combination with scanning tunneling microscopy to determine basic mechanisms in the reactions of atomic and molecular oxygen and chlorine with Si(111) and Si(100). The effect of vibrational excitation was also studied for Cl <sub>2</sub> . We have uncovered a number of reaction mechanisms and determined activation energies and preexponential factors which had not been known previously. Quantitative reaction probabilities for atoms and molecules were determined. they differ from a 10 <sup>3</sup> -10 <sup>5</sup> higher reactivity for O over O <sub>2</sub> to a factor of 2-10 for Cl over Cl <sub>2</sub> . Inhomogeneous decomposition of ultrathin oxides on Si(100) was studied at atomic resolution using STM. It was found that defects at step sites play no role in void nucleation.  DTIC QUANTITY REQUESTED 1			
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## Final Report

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## Completed Work

### 1. *The Reaction of Atomic Oxygen with Si(100) and Si(111): Adsorption, Passive Oxidation and the Effect of Coincident Ion Bombardment.*

The reactions of atomic oxygen with the (100) and (111) surfaces of silicon have been investigated by employing supersonic modulated beam techniques, x-ray photoelectron spectroscopy (XPS), ISS and low-energy ion scattering spectroscopy (ISS). Atomic oxygen adsorbs with unit probability on the clean silicon surface, independent of substrate temperature (110-800 K) and incident mean translational energy (3-16 kcal-mol<sup>-1</sup>). Oxidation of clean silicon with an oxygen atom beam is characterized by two stages: a "fast" stage that corresponds to oxygen chemisorption in the topmost 2-3 silicon layers; and a "slow" stage that corresponds to oxygen incorporation and oxide film growth. The chemisorption stage is described by first-order Langmuirian kinetics with an apparent saturation coverage of approximately 4 ML O( $\alpha$ ), the oxide growth stage by "direct" logarithmic kinetics, where  $d\chi/dt = \alpha \exp(-\chi/L)$ , where  $\chi$  is the oxide thickness. Observation of significant oxidation at substrate temperatures of 110 K suggests that oxide growth in the slow stage may occur by a field-assisted mechanism, where an internal electric field aids transport of oxygen to the underlying silicon substrate layers. XPS and ISS results support of a two-dimensional layer-by-layer growth mechanism for oxidation at substrate temperatures below 900 K. At higher temperatures,  $T_s \geq 1050$  K, oxide growth is three-dimensional involving nucleation and growth of bulk-like oxide islands even for mean coverages as low as 3 ML O( $\alpha$ ). ISS results lend support to the formation of "on-top" adsorbed oxygen atoms that cap silicon dangling bonds at the oxide/gas interface. Coincident bombardment of the silicon substrate with an AR<sup>+</sup> ion beam leads to an enhanced rate of oxidation. The enhancement can be understood in terms of a model involving secondary implantation of adsorbed oxygen atoms, coupled with the simultaneous formation of reactive sites (e.g., dangling bonds, vacancies) for oxygen chemisorption. The effect of coincident ion bombardment is reduced at elevated substrate temperatures (~800 K), since the resulting increased propensity for adlayer rearrangement leads to a decrease in the number of active sites for oxygen chemisorption.

### 2. *Inhomogeneous Decomposition of Ultrathin Oxide Layers on Si(100).*

The thermal decomposition of one monolayer thick oxide films has been investigated using scanning tunneling microscopy (STM). This work is an extension of our early work (see publications 12 and 13 below) using macroscopic techniques in which thicker films could be studied. Because of charging problems, the STM studies were restricted to

monolayer film. We found that inhomogeneous decomposition could be observed with atomic resolution. Voids exposing the bare Si substrate are generated in a film which undergoes no thinning. Voids are not preferentially nucleated at step edges. The density of voids is less than the 4% defect density normally found on well prepared Si(100) - (2x4) surfaces so that the defects, which are known to selectively adsorb oxygen at very low averages, may well be important in the desorption too. A striking result of this work is that we observed a massive reorganization of the surface as the oxygen was desorbed as SiO. This is characterized by a local c(4x4) reconstruction, deep etch pits, a significant defect density which forms (2x2) ordered arrays and an extreme roughening of step edges. This makes the oxygen-silicon system inappropriate for monolayer peeling and suggests that the reaction mechanism is not dominated by a decomposition reaction at the perimeter of voids. We have proposed that the rate limiting step is the generation of a mobile Si monomer which leads to the creation of the observed etch pits.

3. *Development of a Mass Spectrometer for SIMS, Neutral SIMS and Modulated Molecular Beam Studies.*

We have undertaken the development of a quadrupole based analyzer which would allow us to carry out modulated beam kinetic studies and also allow us to characterize surface reaction intermediates using time resolved SIMS. No such analyzer is currently available commercially. We have made considerable success toward this goal. We have inserted an 24 element electrostatic energy analyzer between a quadrupole mass filter and a cross beam ionization source. For residual gas analysis, the sensitivity is 30 % of the value obtained without the analyzer, showing a high degree of ion transmission through the energy filter. We have obtained both SIMS and neutral SIMS spectra by bombarding a stainless steel surface with Ar<sup>+</sup> ions. We observed a very high discrimination between SIMS, neutral SIMS, and residual gas modes which place this analyzer at the top of the field in this category. We are currently working on designing a good extraction lens for the SIMS mode which will improve the sensitivity of this analyzer. It will then be used in our moderated beam experiments.

4. *Thermal and Direct Etching Mechanisms of Si(100) with a Hyperthermal Chlorine Beam.*

The etching of Si(100) with hyperthermal beams of atomic and molecular chlorine has been studied in the temperature range between 130 and 200 K. The dominant etch product, SiCl<sub>4</sub>, is evolved in two parallel reaction pathways, only one of which is thermally activated. We show that the nonactivated pathway, which has an appreciable rate only when hyperthermal chlorine atoms are incident upon the surface, is due to collision induced desorption of weakly bound SiCl<sub>4</sub>. By increasing the normal component of the chlorine incident translational energy, the efficiency of converting incident Cl into SiCl<sub>4</sub> can be increased to 0.6% in the nonthermal channel, at temperatures for which the thermal etching rate is negligible. The normal energy scaling and the observed energy threshold suggest that this process should result in highly anisotropic etching.

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5. *Etching of Si Surfaces with Hot Chlorine Beams: Translational and Vibrational Excitation of the Incident Chlorine Particles.*

A systematic study of etching of Si(100) and Si(111) and Ar<sup>+</sup> bombarded Si(100) (surface with defect sites), with chlorine has been carried out. We have compared the reactivity of atomic and molecular chlorine, and studied the effect of translational and vibrational excitation of the etchant on the etch rate. Similar etch rates were obtained on the Si(100) and Si(111) single crystal surfaces. On both surfaces the major etch products were SiCl<sub>4</sub> at T<sub>s</sub> < 500 K and SiCl<sub>2</sub> at T<sub>s</sub> > 600 K. Some SiCl desorption was obtained at T<sub>s</sub> > 1100 K. We have outlined the conditions under which the etch rate, at constant incident flux, is adsorption and desorption limited. On the Si(100) and Si(111) surfaces we found that when the etch rate is reaction limited, higher etch rate can be obtained with atomic chlorine than with molecular chlorine. In the adsorption limited regime, translational excitation of both atomic and molecular chlorine results in a higher etch rate than that obtained with slow atomic and molecular chlorine. Vibrational excitation of Cl<sub>2</sub> does not result in an enhancement of the etch rate on the single crystal surfaces studied. In the desorption limited regime the etch rate is primarily determined by the surface temperature. The nature of the etchant particles does not have a significant effect. On Ar<sup>+</sup> bombarded Si(100), we obtained a small increase in the etch rate with translationally and vibrationally excited Cl<sub>2</sub>, and comparable enhancement is obtained with Cl<sub>2</sub> that is only translationally excited. The difference in the etch properties of the single crystalline and Ar<sup>+</sup> bombarded silicon surfaces points to the importance of surface defects in etching. The present results show that at room temperature the low etch rate of silicon single crystal surfaces with chlorine, as compared to etching with fluorine, is due to the low formation rate of volatile surface products.

6. *Reactions of Chlorine with Si(100) and Si(111): Adsorption and Desorption Kinetics.*

Adsorption of atomic and molecular chlorine on the Si(100) and Si(111) surfaces, and the desorption kinetics of the formed Chlorosilicon species have been investigated. The saturation coverage after Cl<sub>2</sub> exposure is 1.0 ± 0.1 ML on Si(100) and 1.4 ± 0.1 ML on Si(111), while in atomic chlorine exposure the uptake slows down considerably above ~5 ML on both surfaces. The desorption kinetics of the major chlorosilicon products, SiCl<sub>2</sub> and SiCl<sub>4</sub>, is first order in chlorine coverage under 850 K. Above 900 K the SiCl<sub>2</sub> desorption kinetics is different on Si(111) and Si(100). Desorption of SiCl<sub>2</sub> above 900 K from Si(111) is second order in chlorine coverage. From the Si(100) surface above 900 K the SiCl<sub>2</sub> desorption rate is first order at 0.1 ML < θ<sub>Cl</sub> < 0.4 ML, increases steeply at ~0.5 ML and become zero order and negative order in chlorine coverage as the saturation coverage (1.0 ML) is approached. The second order kinetic parameters extracted for SiCl<sub>2</sub> desorption from Si(111) above 950 K at θ<sub>Cl</sub> ~0.3 ML are v<sub>d</sub> = 2000 cm<sup>2</sup>/sec and E<sub>d</sub> = 83 kcal/mol. When empty surface sites are available, desorption of SiCl<sub>n</sub> (n > 1) is accompanied by dissociation of some of the SiCl<sub>n</sub> on the surface to form SiCl(ads).

### Cumulative Publications to Date

1. Molecular Beam Studies of the Reaction of Silicon with Oxygen, M.P. D'Evelyn, M.M. Nelson and T. Engel, *J. Vac. Sci. Technol.* A5(1987), 642.
2. Kinetics of the Adsorption of O<sub>2</sub> and of the Desorption of SiO on Si(100): A molecular Beam, XPS and ISS Study, M.P. D'Evelyn, M.M. Nelson and T. Engel, *Surface Science*, 186 (1987) 75.
3. Thermal Decomposition of a Silicon-Fluoride Adlayer: Evidence for Spatially Inhomogeneous Removal of a Single Monolayer of the Silicon Substrate, J.R. Engstrom, M.M. Nelson and T. Engel, *Phys Rev.* B 37 (1988), 6563.
4. The Adsorption and Reaction of Fluorine on the Si(100) Surface, J.R. Engstrom, M.M. Nelson and T. Engel, *Surface Science*, 215 (1989), 437.
5. Reactive Atom-Surfacing Scattering: The Adsorption and Reaction of Atomic Oxygen on the Si(100) Surface, J.R. Engstrom, M.M. Nelson and Thomas Engel, *J. Vac. Sci. Technol.* A7 (1989), 1837.
6. Ion Bombardment Assisted Adsorption of Oxygen on Si(100), J.R. Engstrom, D. Bonser and T. Engel, *Appl. Phys. Lett.* 55 (1989), 2202.
7. Atomic Versus Molecular Reactivity at the Gas-Solid Interface: The Adsorption and Reaction of Atomic Oxygen on the Si(100) Surface, J.R. Engstrom and T. Engel, *Phys. Rev.* B41 (1990) 1038.
8. The Reaction of Atomic Oxygen with Si(100) and Si(111): I. Oxide Decomposition, Active Oxidation and the Transition to Passive Oxidation, J.R. Engstrom, D.J. Bonser, M.M. Nelson and T. Engel, *Surface Science*, 256 (1991) 317.
9. Direct Chemical Evidence of Spatial Inhomogeneity in Decomposition of Silicon Oxide Overlayers on Si(100), Y.-K. Sun, D.J. Bonser and T. Engel, *Physical Review*, B43 (1991) 14309.
10. The Reaction of Atomic Oxygen with Si(100) and Si(111): II. Adsorption Kinetics and Ion Assisted Reaction Kinetics, J.R. Engstrom, D.J. Bonser, M.M. Nelson and T. Engel, *Surface Science*, 268 (1992) 238.
11. The Thermal Decomposition of Ultrathin Oxide Layers on Si(100), Y.-K. Sun, D.J. Bonser and T. Engel, *J. Vac. Sci. Technol.* A10 (1992) 2314.
12. Direct Measurement of Reaction Kinetics for the Decomposition of Ultrathin Oxide on Si(100) Using Scanning Tunneling Microscopy, K.E. Johnson and T. Engel, *Phys. Rev. Lett.* 69 (1992) 339.
13. The Mesoscopic and Microscopic Structural Consequences from Decomposition and Desorption of Ultrathin Oxide Layers on Si(100) Studied by Scanning Tunneling

Microscopy, K.E. Johnson, P.K. Wu, M. Sander and T. Engel, *Surface Science*, 290 (1993) 213.

14. The Interaction of Molecular and Atomic Oxygen with Si(100) and Si(111), Thomas Engel, *Surface Science Reports*, 18 (1993) 91.
15. Thermal and Direct Etching Mechanisms of Si(100) with a Hyperthermal Chlorine Beam, A. Szabo, P. Farrall and T. Engel, *J. Appl. Phys.*, in press.
16. Etching of Si Surfaces with Hot Chlorine Beams: Translational and vibrational Excitation of the Incident Chlorine Particles, A. Szabo and T. Engel, submitted to *J. Vac. Sci. Technol.*
17. Reactions of Chlorine with Si(100) and Si(111): Adsorption and Desorption Kinetics, A. Szabo, P. Farall and T. Engel, submitted to *Surface Science*.